

Performance and Safety Evaluations of Moli Spinel Lithium-ion Cells

Judith Jeevarajan

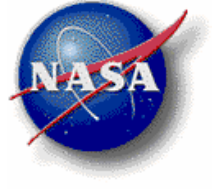
Joe Cook

Jacob Collins

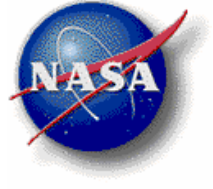
NASA- JSC

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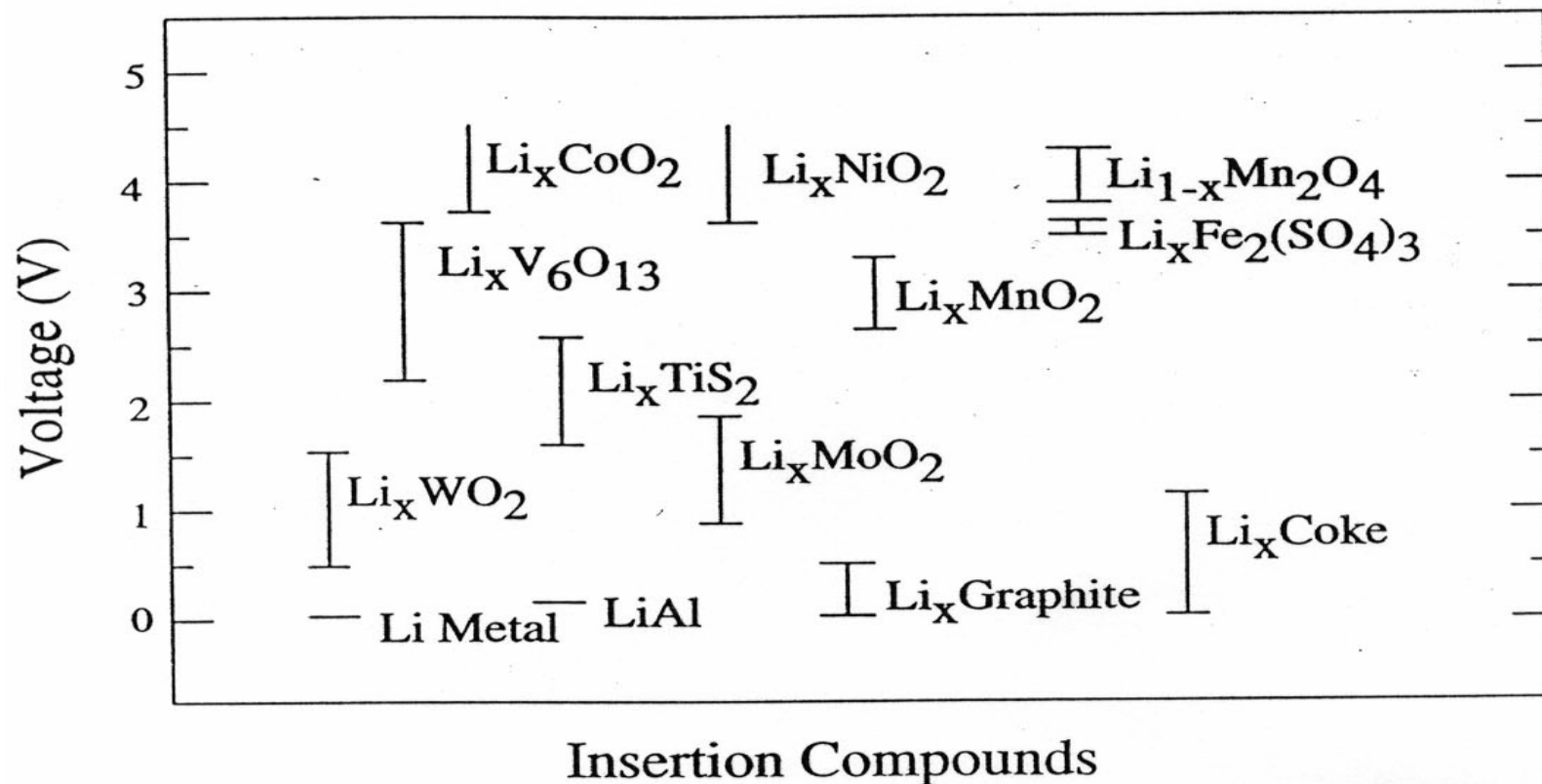
- **Introduction**
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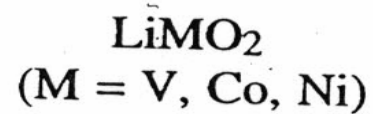
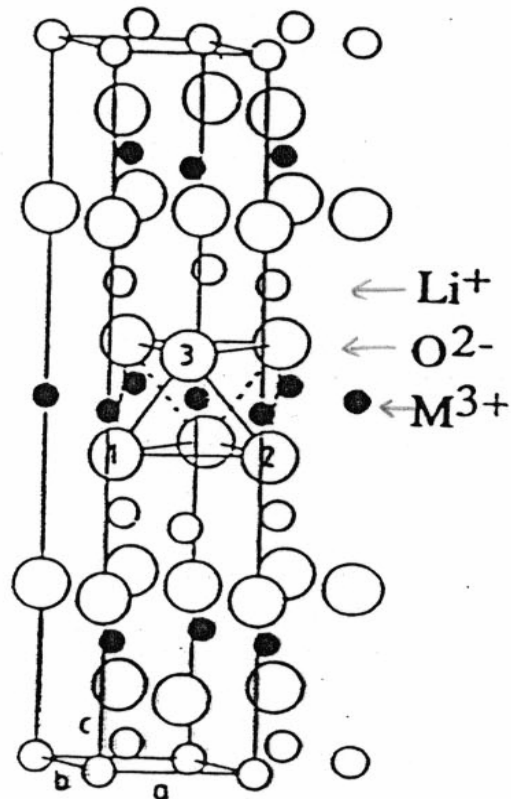
Introduction

- LiMn_2O_4 is a spinel oxide.
- Co and Ni are more expensive and toxic than Mn.
- Performance of the LiMO_2 is influenced strongly by the ordering of the Li^+ and M^{3+} ions.
- Cation disordering is a major drawback in LiCoO_2 cathodes. Presence of Co in the Li planes leads to the extraction of Co into the solution leading to higher levels of cell failure.
- However, LiMn_2O_4 exhibits capacity fading. Due to the Jahn-Teller distortion associated with the Mn^{3+} ions.

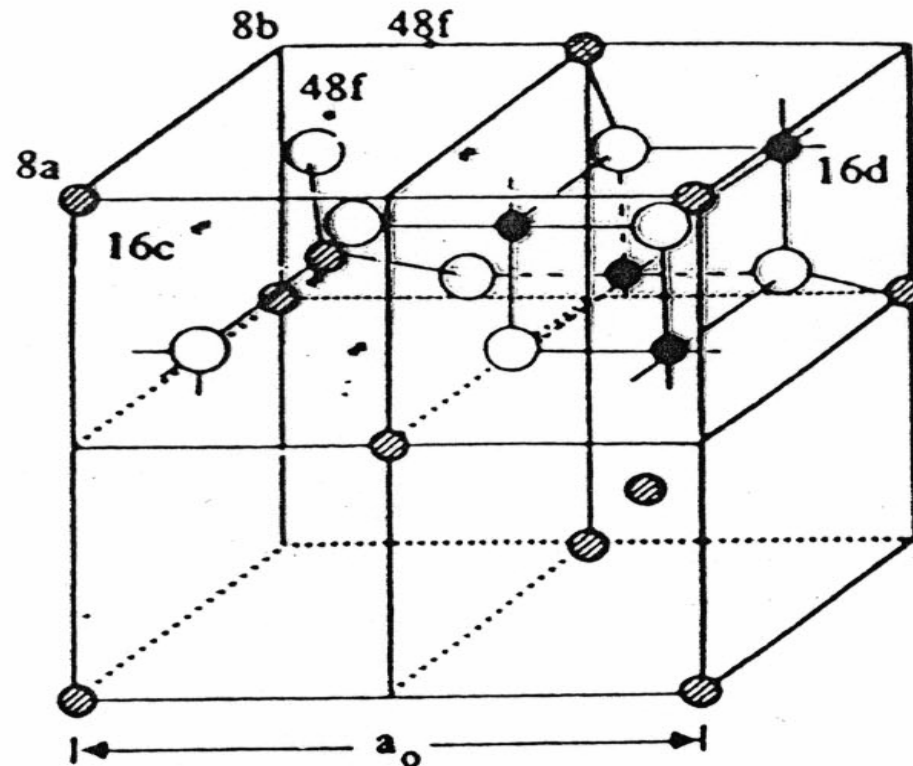
Electrode Potential Ranges of Lithium Insertion Compounds



LAYERED (2-D) LiMO_2 ($M = \text{Co}, \text{Ni}$)

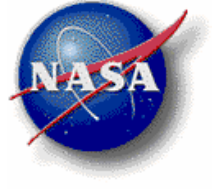


SPINEL (3-D) LiMn_2O_4





Physical and Electrochemical Characteristics



Physical Characteristics:

Diameter: 18 mm

Height: 65 mm

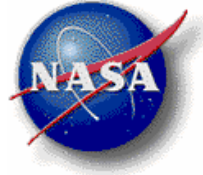
Weight: 41.8 g

Electrochemical Characteristics:

OCV: 3.88 V (as recd.)

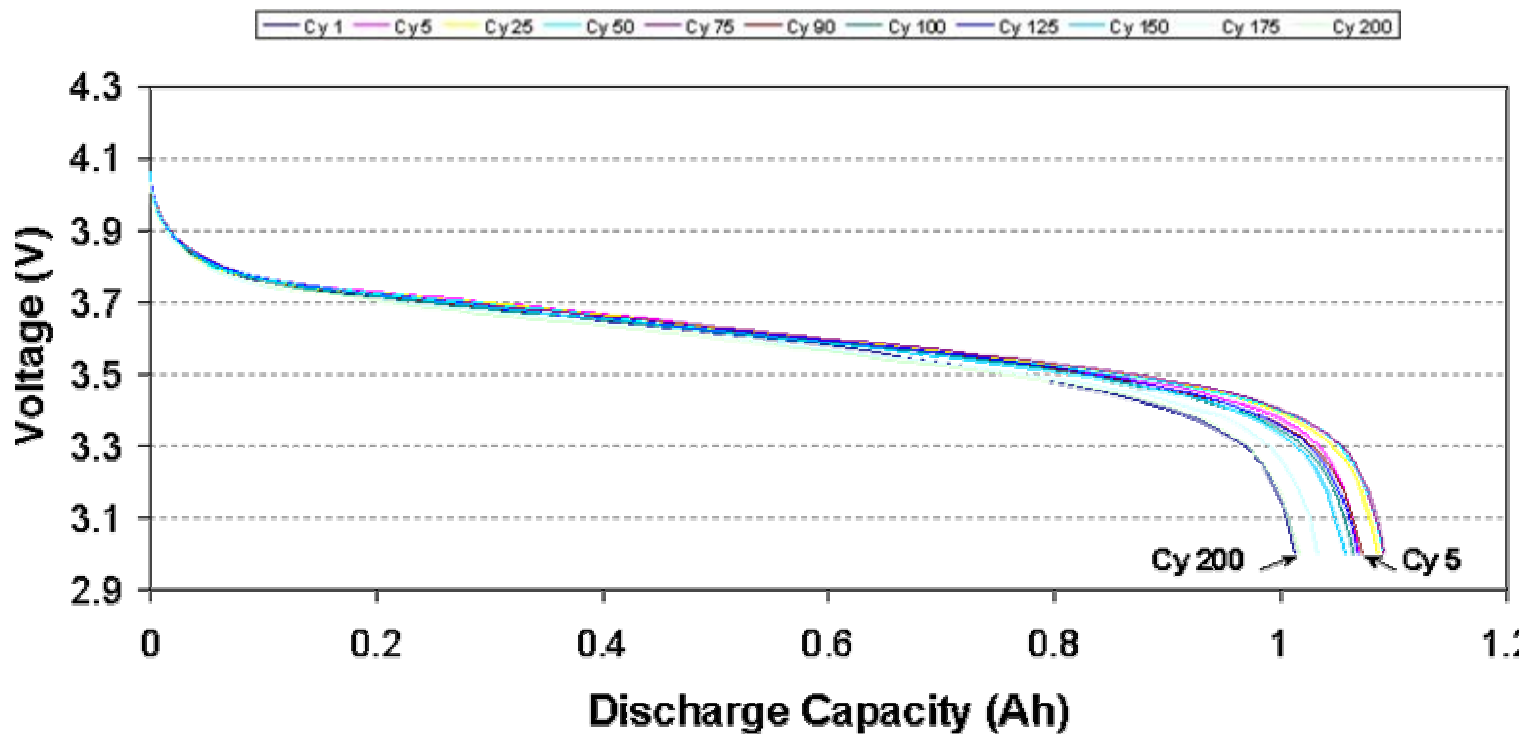
CCV: 3.5 V

Capacity: 1.27 Ah (1.4 Ah)



Typical Discharge Profiles for the Moli Spinel 18650 Cell

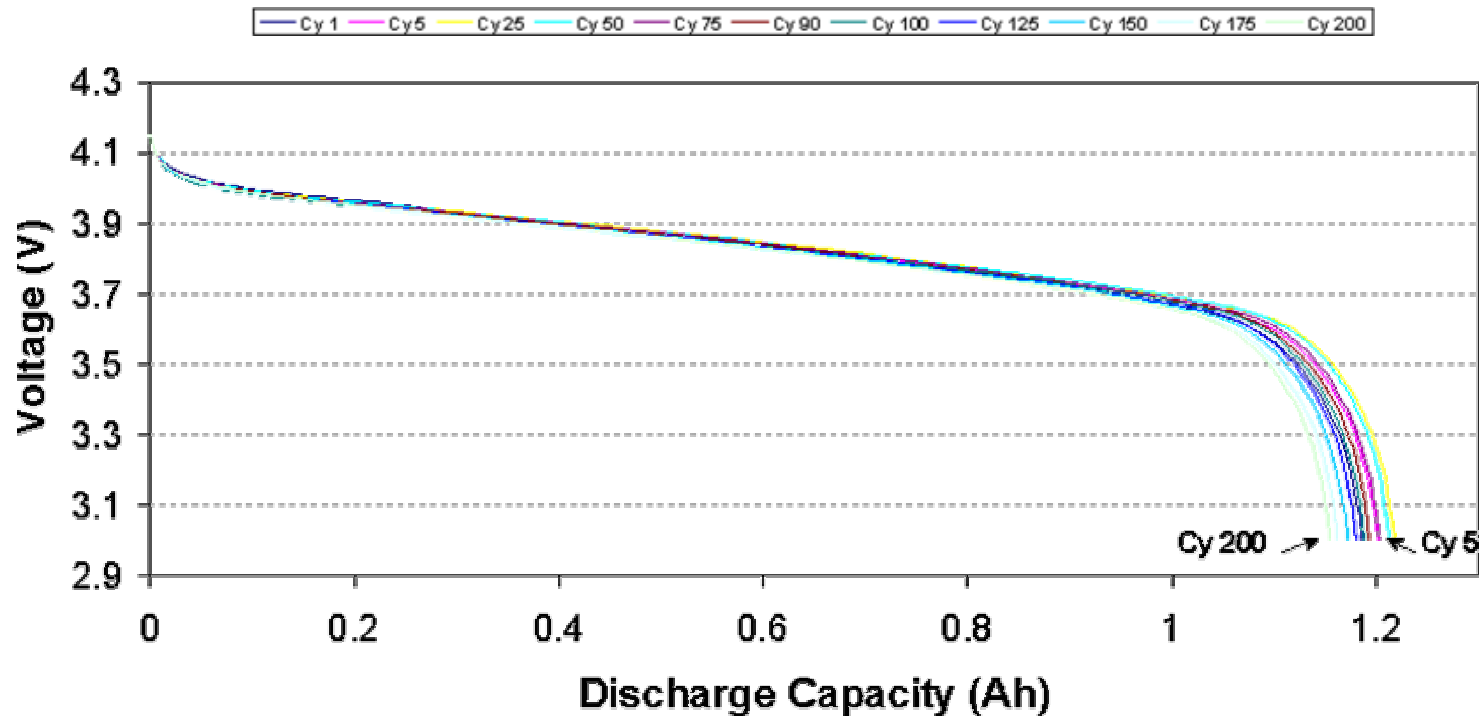
Figure A1.2 - Voltage vs. Discharge Capacity of Moli Spinel 18650 Li-Ion Cell
For 1C Rate Charge to 4.2V with Taper to 50mA and -1C Rate Discharge to 3.0V

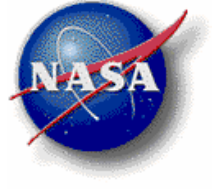




Typical Discharge Profiles for the Moli Spinel 18650 Cell

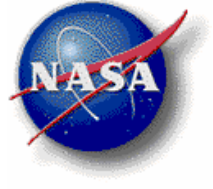
Figure A3.2 - Voltage vs. Discharge Capacity of Moli Spinel 18650 Li-Ion Cell
For 1C Rate Charge to 4.2V with Taper to 50mA and -0.25C Rate Discharge to 3.0V





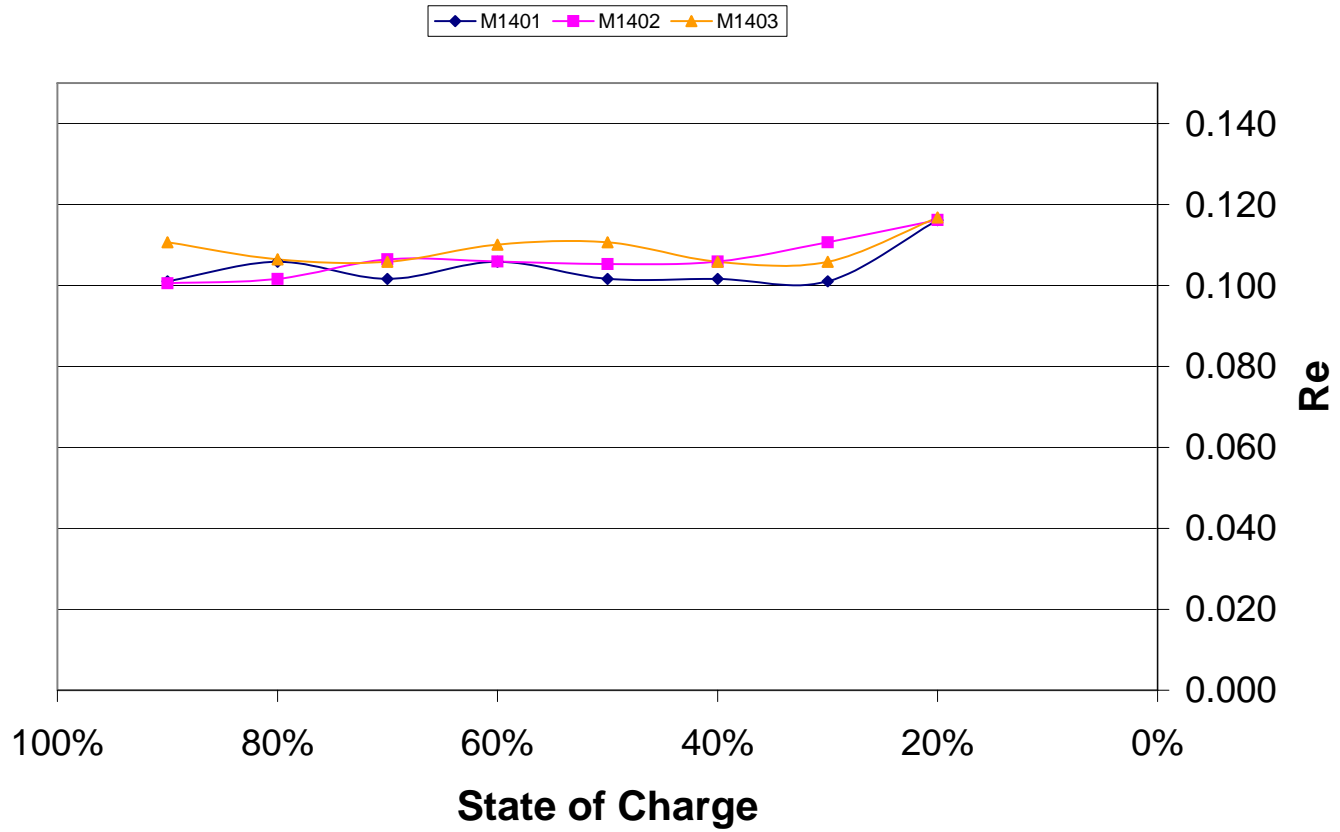
Summary of Rate Capability Tests

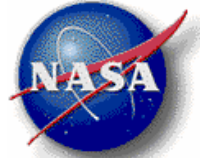
Charge/ Discharge Rate	Capacity 5 th Cycle [Ah]	Capacity 200 th Cycle [Ah]	Capacity Change [Ah]	% Capacity Change
1C/1C	1.071	1.023	-0.048	4.5 %
1C/0.5 C	1.173	1.117	-0.056	4.8 %
1C/0.25 C	1.202	1.154	-0.048	4.0 %
0.5 C/1C	1.044	1.034	-0.010	0.95 %
0.5 C/0.5 C	1.156	1.117	-0.039	3.4 %
0.5 C/0.25 C	1.188	1.134	-0.054	4.5 %
0.25 C/1 C	1.049	1.046	-0.003	0.3 %
0.25 C/0.5 C	1.187	1.097	-0.090	7.6 %
0.25 C/0.25 C	1.191	1.108	-0.083	6.9 %



Internal Resistance vs SOC for the Moli Spinel 18650 Li-ion Cells

Figure 3 - Effective Internal Resistance of Moli 18650 Li-Ion Cells

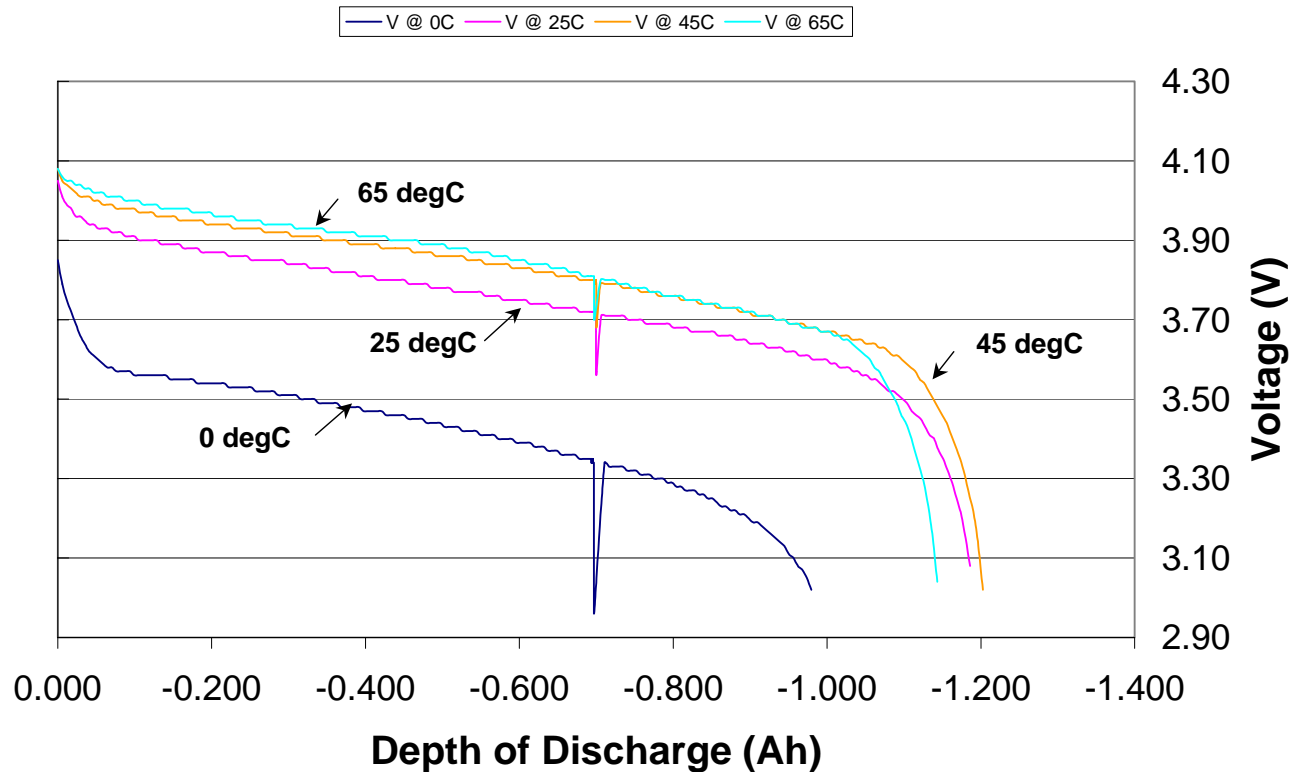


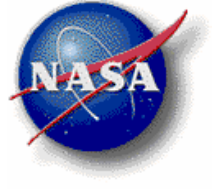


Performance of the Moli Spinel 18650 Li-ion Cells at Different Temperatures

Figure 7 - Voltage vs. Discharge Capacity Curves of Moli 18650 Li-Ion Cells
For 0.5C Rate Charge at +25C and -0.5C Rate Discharge at Different Temperatures

R_e :
0 °C : 0.079 ohm
25 °C: 0.083 ohm
45 °C: 0.117 ohm
65 °C: 0.264 ohm

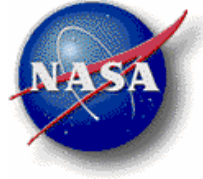




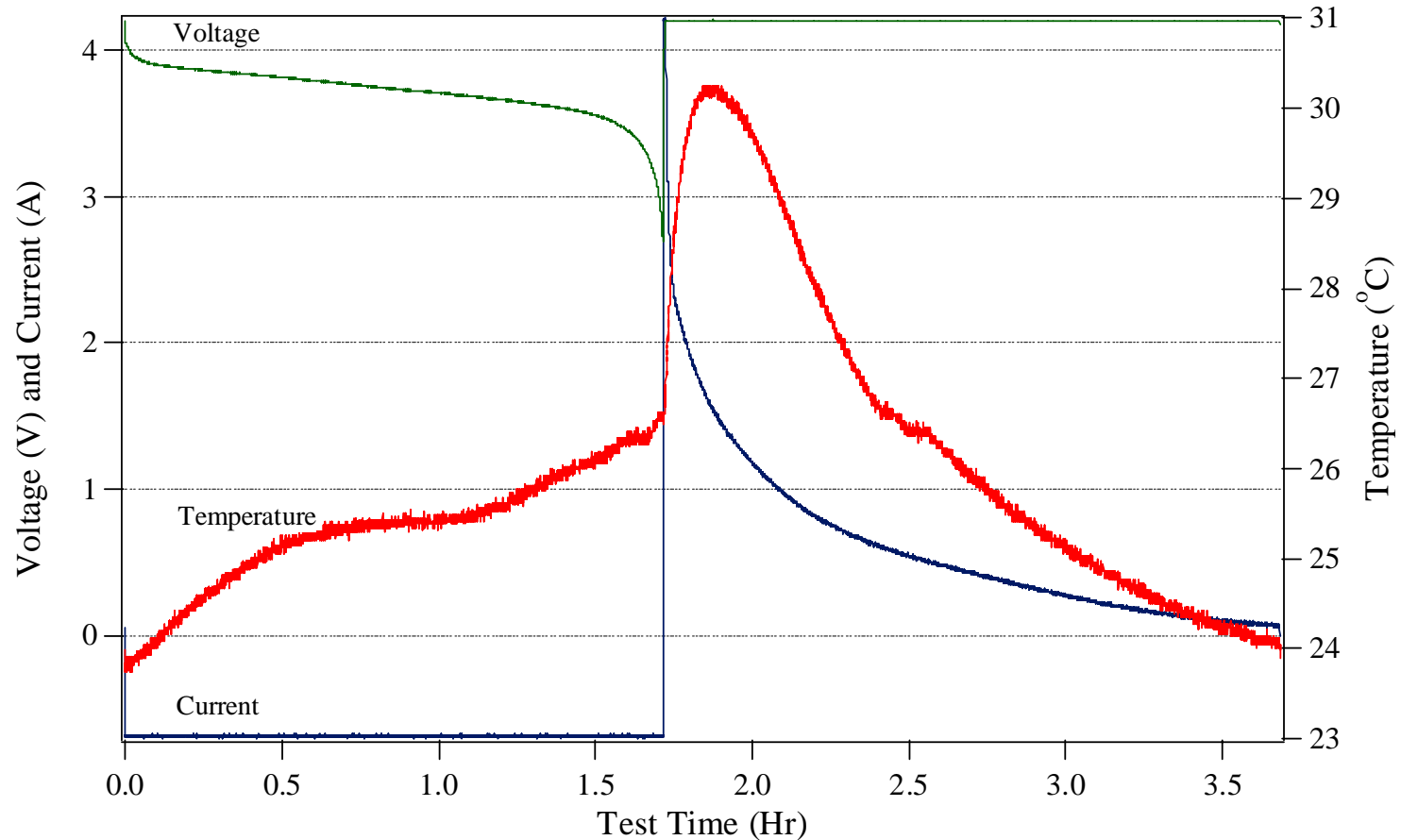
Abuse Tests



Fast Charge Test of the Moli Spinel 18650 Cells

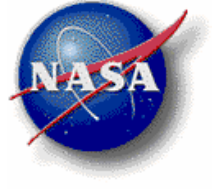


3C charge to 4.2 V with current taper/discharge with 0.5 C rate to 2.7 V

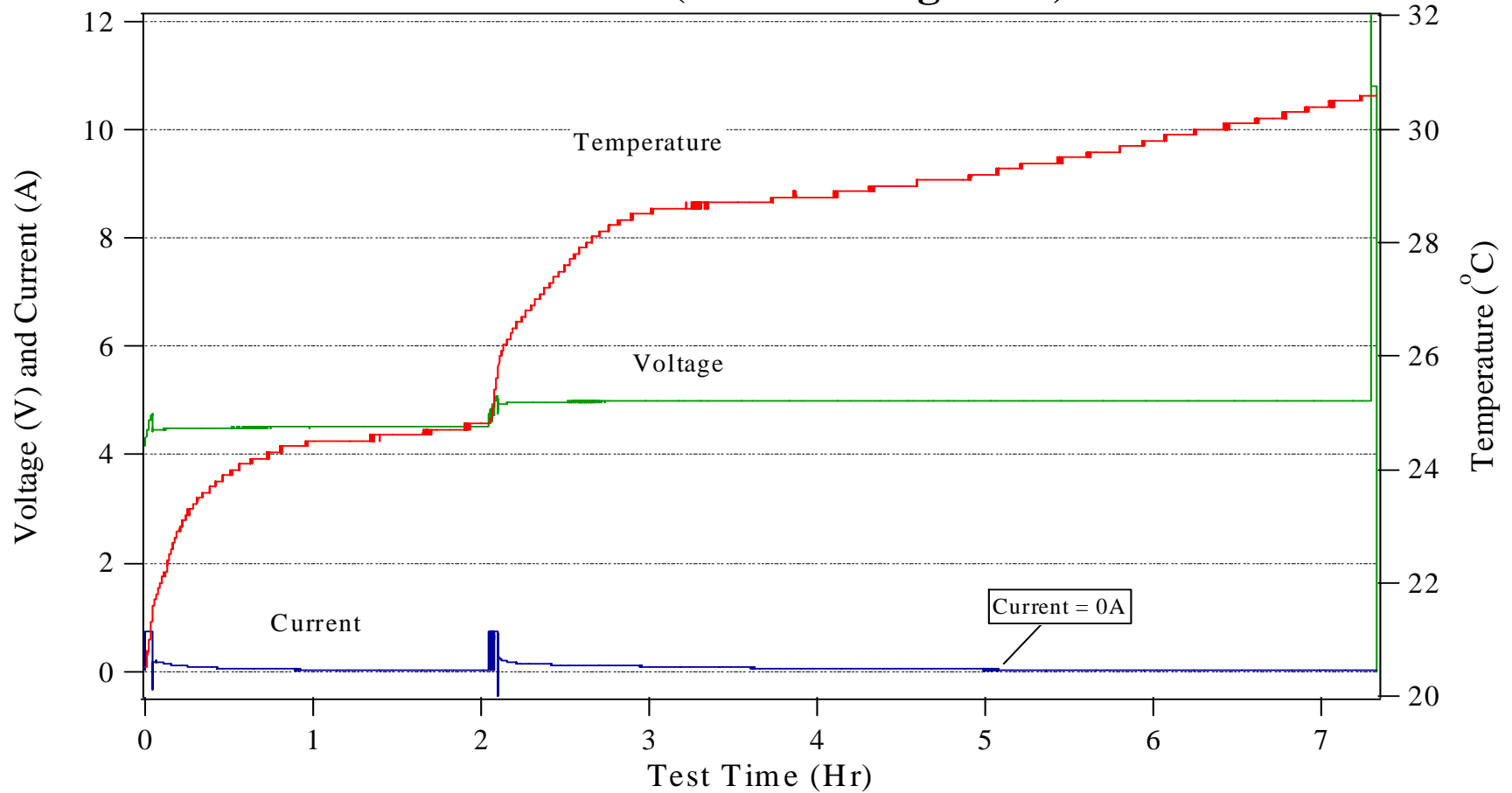




Overvoltage Test on the Moli Spinel 18650 Cells

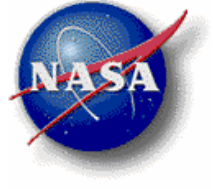


CID activation (0.7 Ah charge rate)

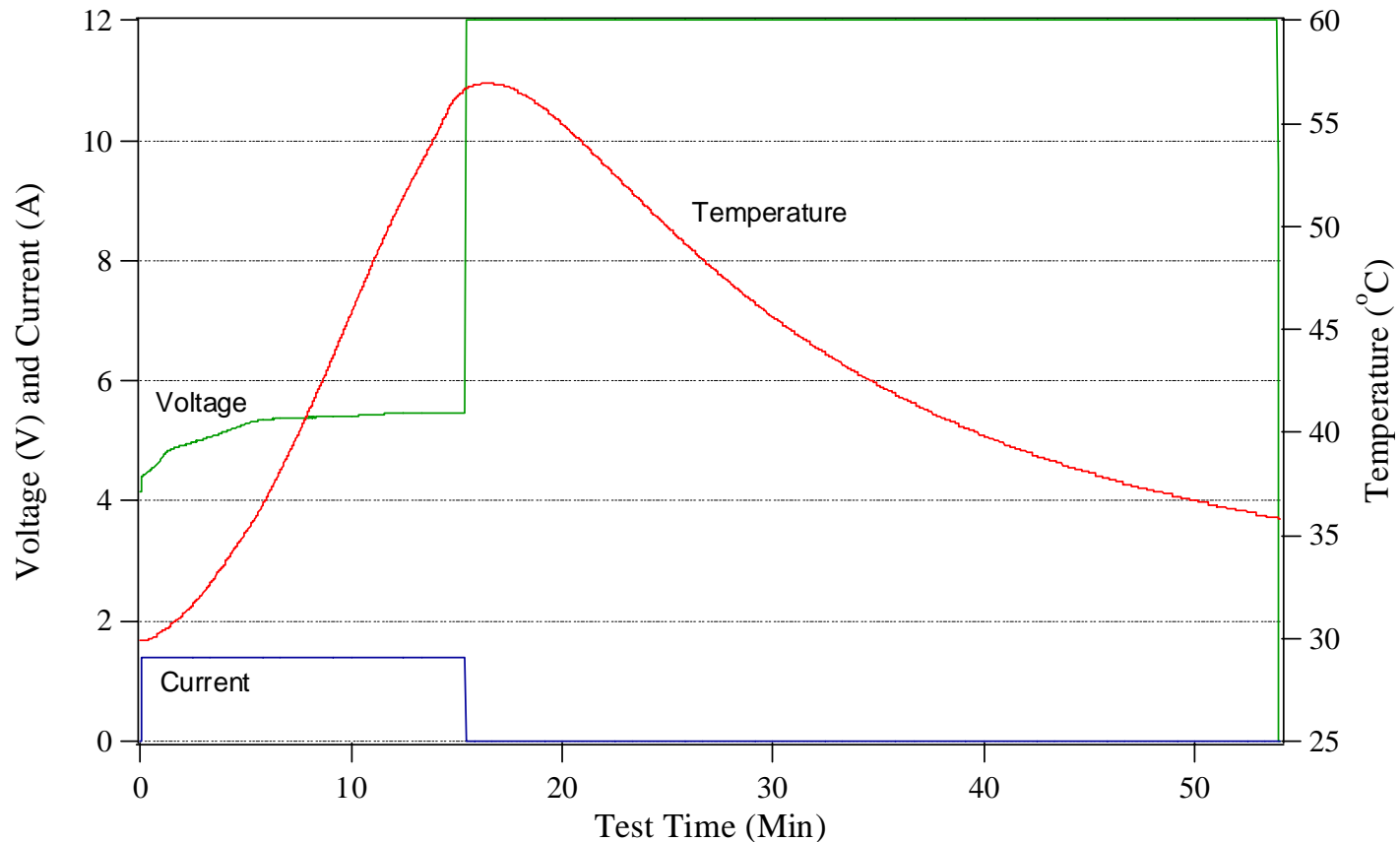


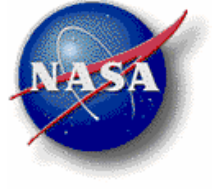


Overcharge of the Moli Spinel Cells to 12 V for 50 minutes



1C charge rate; CID activation in 15 minutes; Max temp: 57 °C



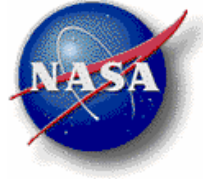


Overcharge to 12 V on the Moli Spinel Cells

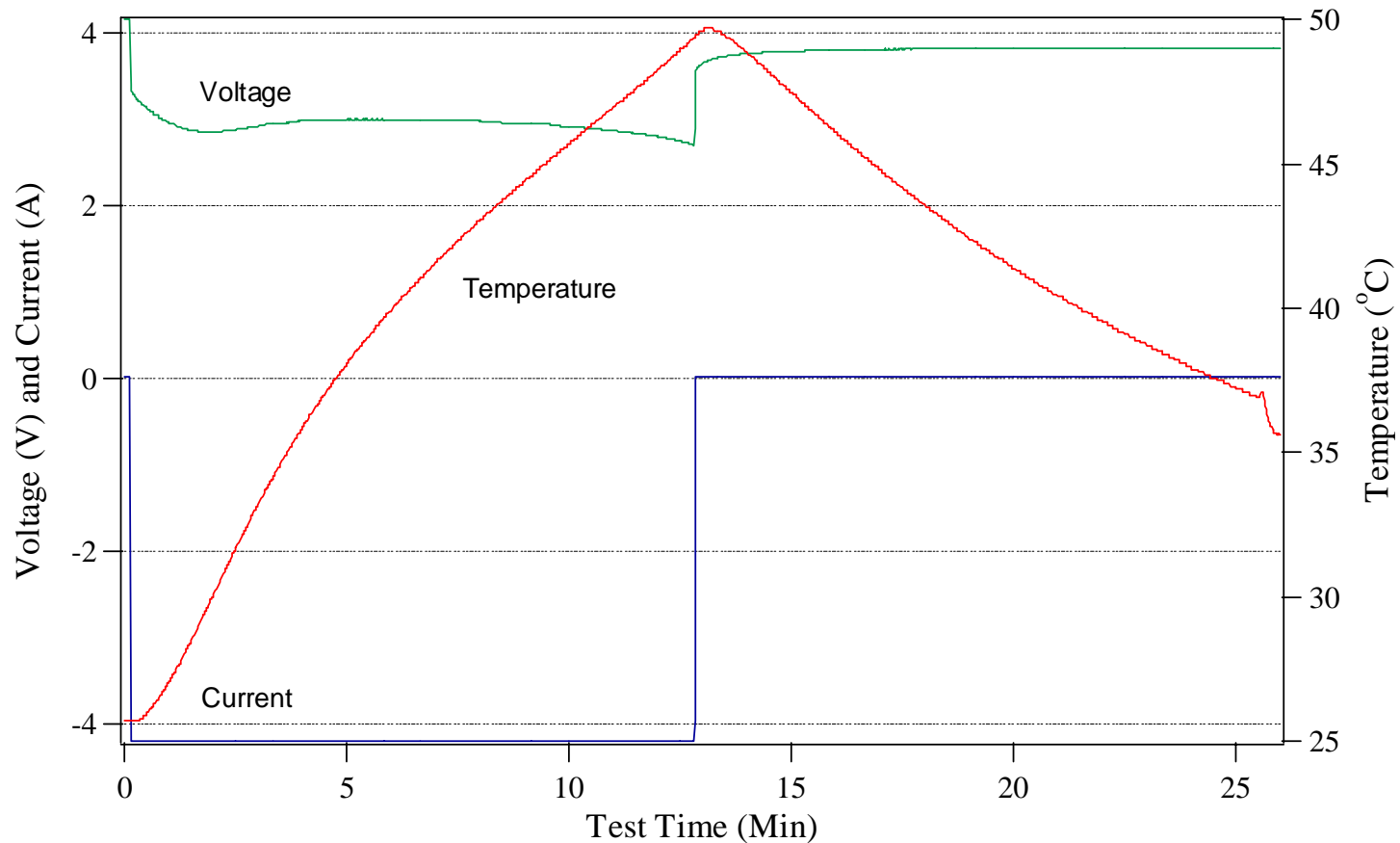
- **Charge with C/5 current to 12 V for 50 minutes**
No occurrences; max temp: 37 °C
- **Charge with C/2 current to 12 V for 50 minutes**
CID activation occurred at approximately 30 minutes; max temp: 43 °C
- **Charge with 2 C current to 12 V for 50 minutes**
CID activation occurred in 7 minutes; max temp. 78 °C

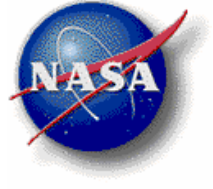


Fast Rate Discharge Test on the Moli Spinel 18650 Cells



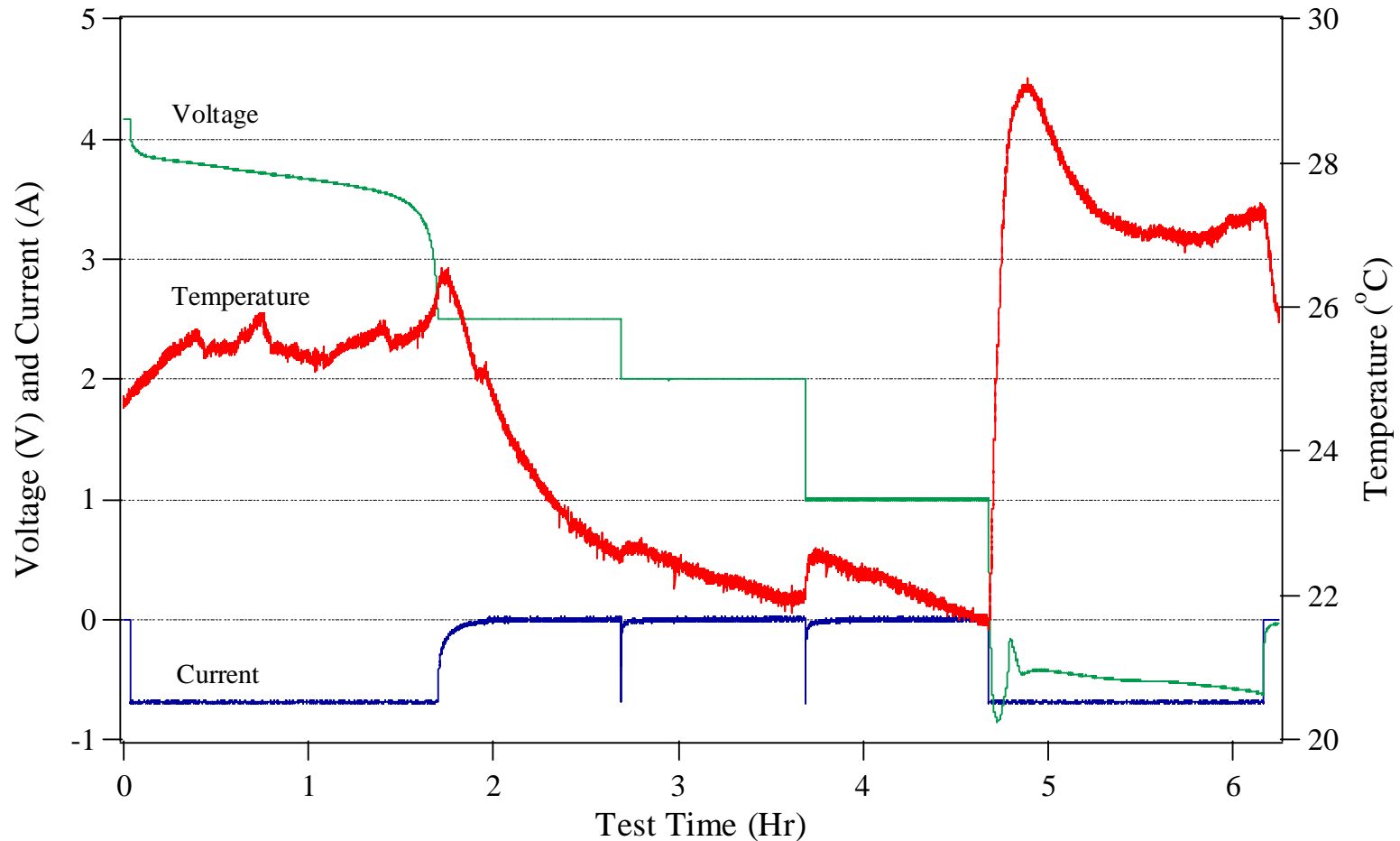
3C current discharge to 2.7 V; cap: 0.9 Ah; max temp. 50 °C

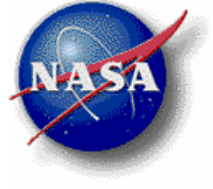




Overdischarge into Reversal Test of the Moli Spinel 18650 Li-ion Cells

Discharge: 0.5 C; max temp: 29 °C



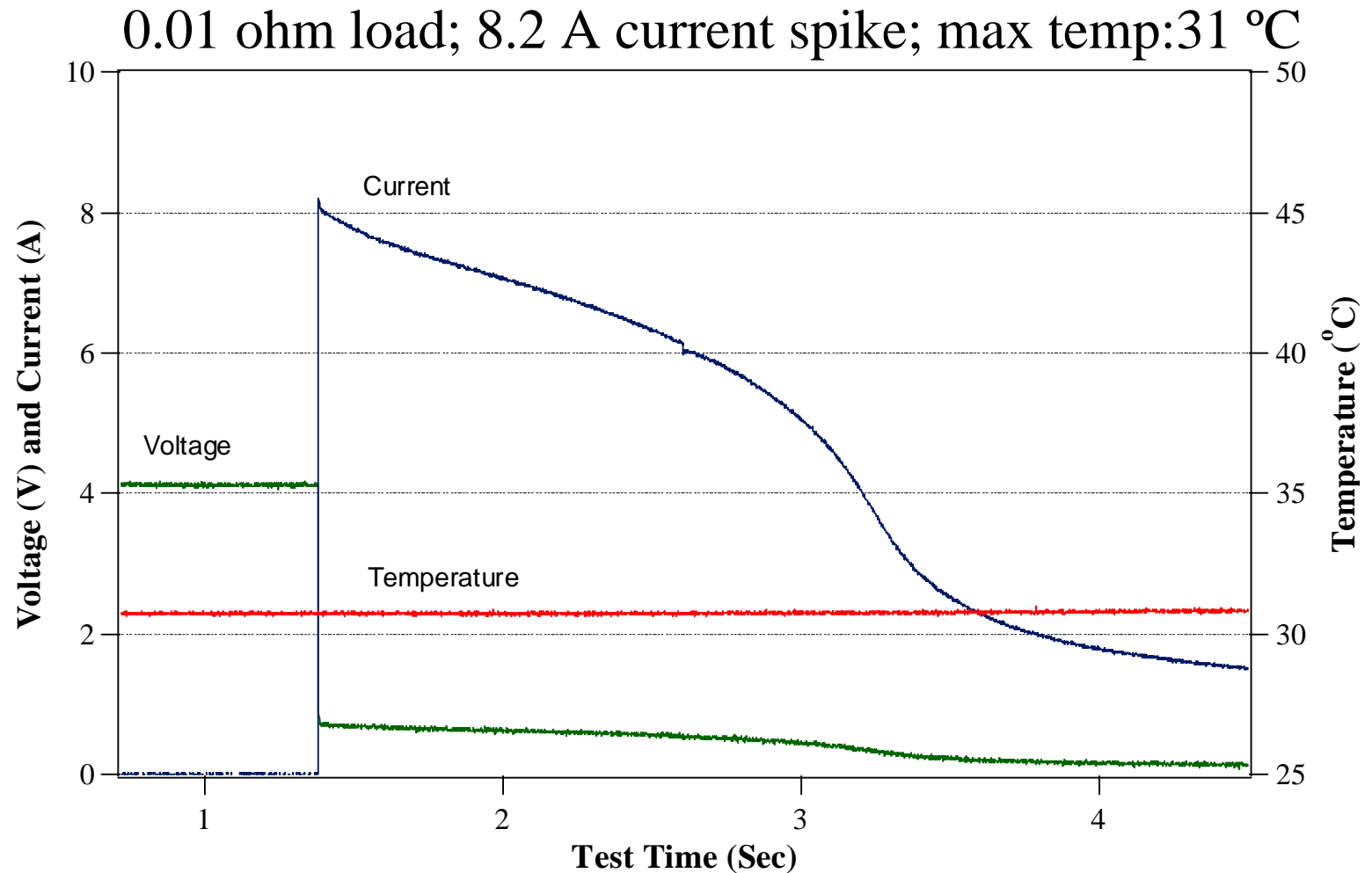
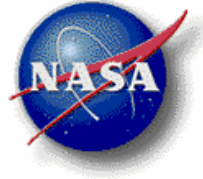


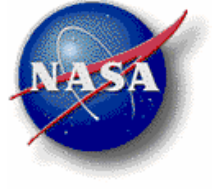
Overdischarge into Reversal on the Moli Spinel 18650 Li-ion Cells

- Discharge current: 1C; max temp: 40 °C
- Discharge current: 2C; max temp: 50 °C



External Short Circuit Test on the Moli Spinel 18650 Cells



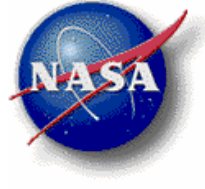


External Short Circuit Test on Moli Spinel 18650 li-ion Cells

- 0.05 ohm load; 5.8 A current spike, max temp: 35 °C
- 0.01 ohm load to cells charged to 50 % SOC; 8 A current spike; no significant changes in temp.



Simulated Internal Short/Crush Test on the Moli Spinel 18650 Li-ion Cells



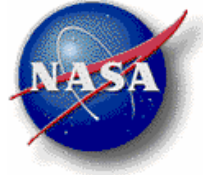
Fully charged cells: max temp: 77 °C
(electrolyte leakage; no venting or fire)

50 % charged cells: max temp: 57 °C (no venting or fire)

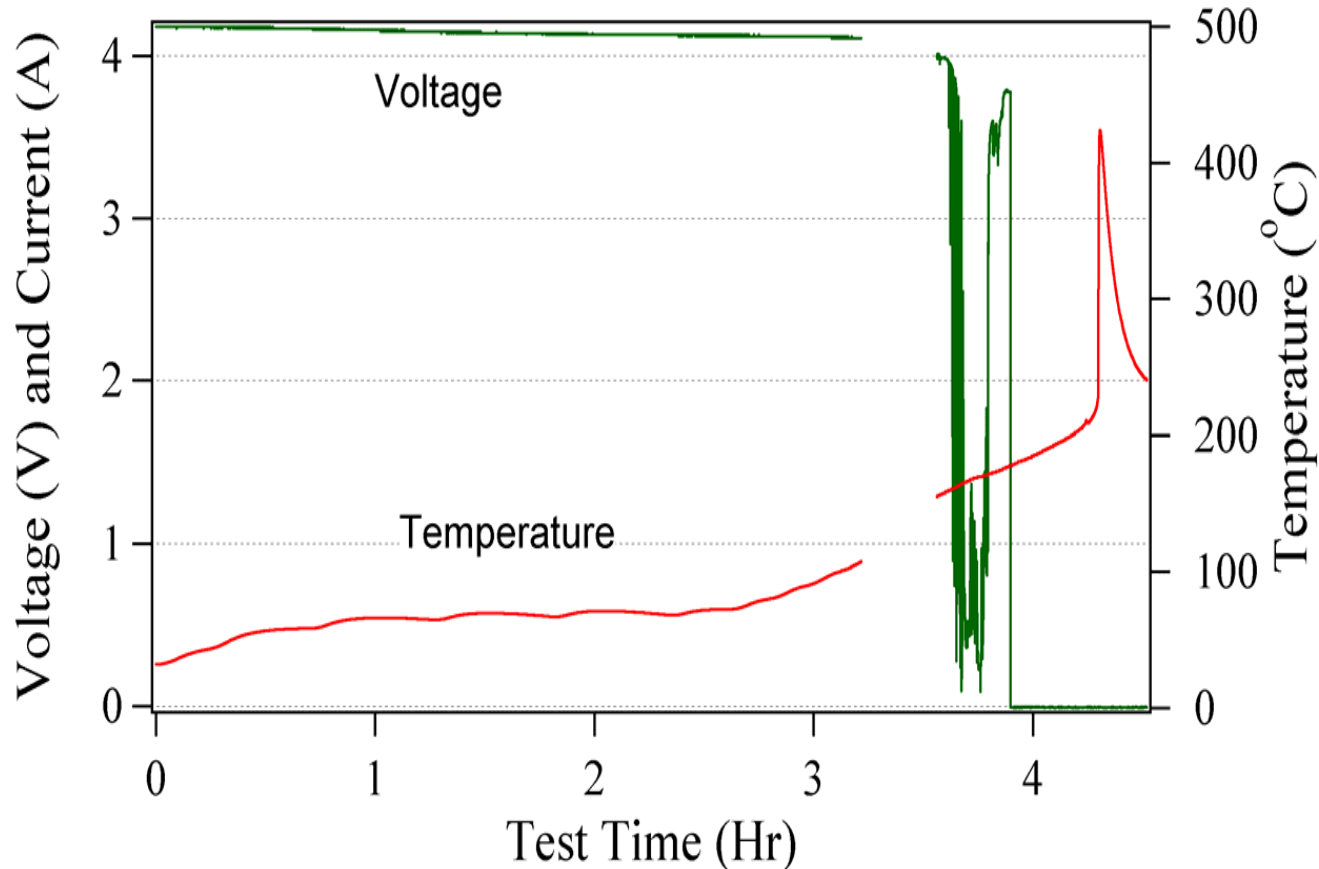




Heat-to-vent Test on the Moli Spinel 18650 Li-ion Cells

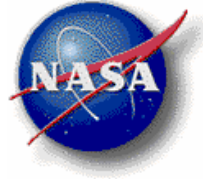


100 % charged cells: Onset of thermal runaway: 217 °C; max
temp 424 °C

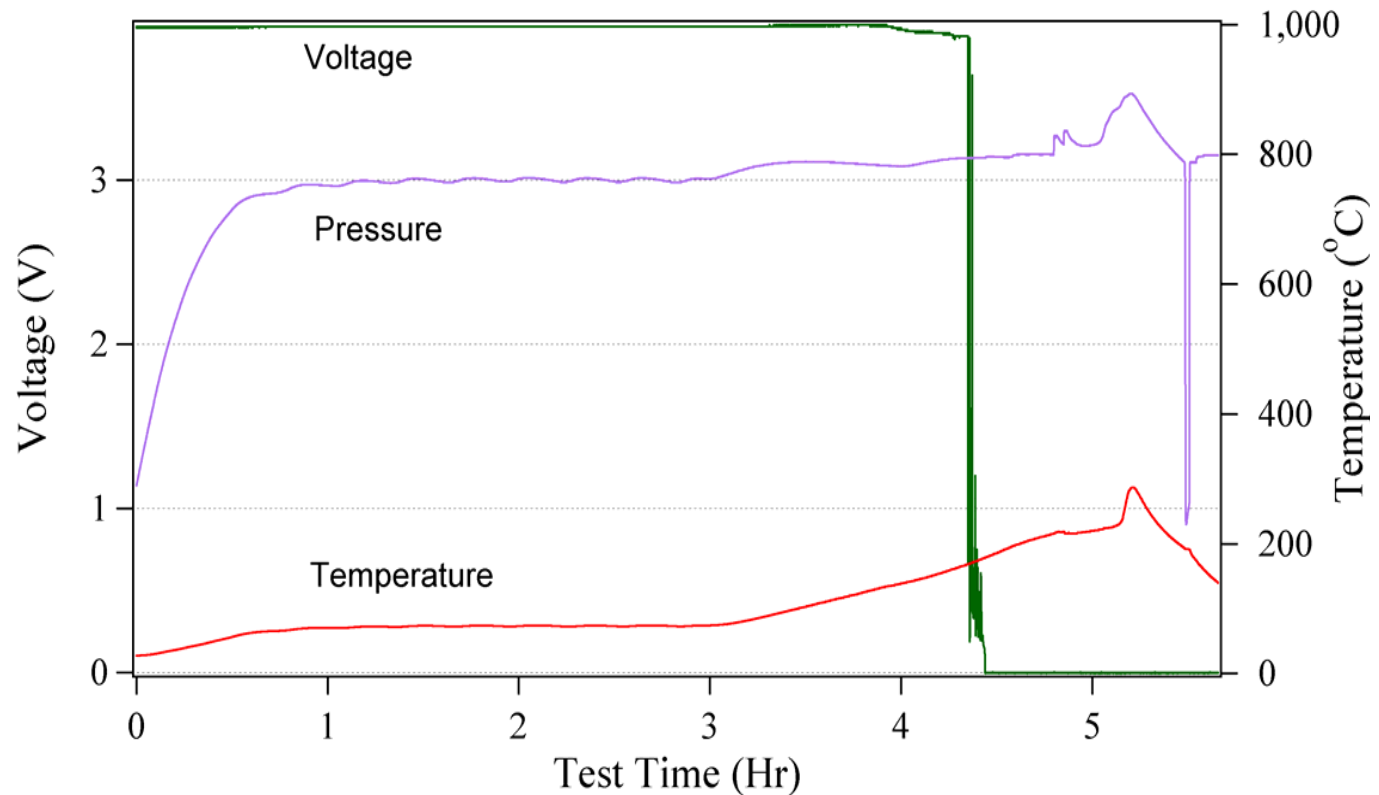


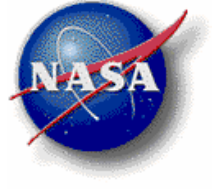


Heat-to-vent Test on the Moli Spinel 18650 Li-ion Cells



50 % charged cells: Voltage drop at 168 °C; max temp 287 °C; no rapid increase in temp.





Vibration of Moli Spinel 18650 li-ion cells

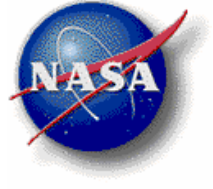
20 to 80 Hz + 3 db/oct

80 to 350 Hz 0.1 g²/Hz

350 to 2000 Hz - 3 db/oct

15 minutes in each independent axis.

No change in capacity on subsequent cycling of the cells.

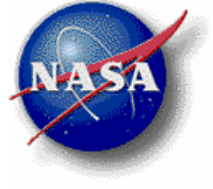


Drop Test on the Moli Spinel 18650 Li-ion Cells

Drop from 6 ft. Cells gained 11 % capacity after the drop.



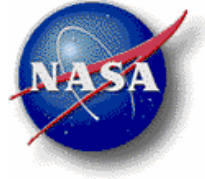
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Vent and Burst Pressure Test on Moli Spinel Li-ion Cells

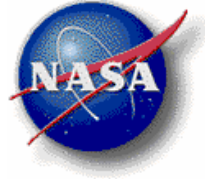
Vent Pressure: 250 psi-300 psi

Burst Pressure: 1650 psi



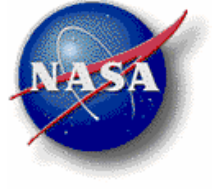
Conclusions

- **Moli spinel cells show similar performance under the rate protocols tested.**
- **The R_e for the cells varies between 100 and 120 mohms for the cells.**
- **The overcharge on the cells shows that the cells do not perform well under fast charge conditions.**
- **Under conditions of high rate overcharge, the CID gets activated faster than under low charge rates.**
- **The fast rate discharge shows that the cells can tolerate it.**
- **The overdischarge into reversal tests show that the cells die benignly.**



Conclusions

- **The current spike obtained during the hard external short test is small (8.2 A) compared to those obtained from a LiCoO_2 system (60 to 80 A).**
- **The simulated internal short did not result in an explosion or fire as it does with the LiCoO_2 systems.**
- **The temperatures obtained during the heat-to-vent test are not very high compared to the cobaltate cells.**
- **The cells do not retain capacity very well, but the capacity can be recovered with cycling.**
- **The spinel cells are much safer under abuse conditions than the lithium-ion cells with other transition metal oxides.**



Acknowledgment

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